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# The modeling of reactive solute transport with sorption to mobile and immobile sorbents

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## Abstract

This paper presents a mathematical model to describe the transport of reactive solutes with sorption to mobile and immobile sorbents. The mobile sorbent is considered to be reactive, too. The sorption processes mentioned are equilibrium and nonequilibrium processes. A transformation of the model in terms of total concentrations of solute and mobile sorbents is presented which simplifies the mathematical formulation. Effective isotherms, which describe the sorption to the immobile sorbent in the presence of a mobile sorbent and rate functions are introduced and their properties are discussed. The differences to existing approaches to model reactive solute transport are shown. Possible extensions are pointed out and the numerical approximation is sketched. The restrictions of the model as a consequence of the assumptions made on reactive solute transport are not due to mathematical reasons, but due to limitations of experimental information available.

# INTRODUCTION

Dissolved organic carbon (DOC) in soils and aquifers is considered as a sorbent and carrier for organic contaminants. The knowledge of the interaction between hydophobic organic chemicals (HOC) and soil or aquifer materials in the presence of mobile carriers, such as DOC, plays an important role in understanding of the transport behavior of the HOC. Several studies focused on the influence of the chemical characteristics of the contaminant on solubility enhancement by DOC [*Kile and Chiou*, 1989]. Enhanced transport of pesticides and hydrophobic organic chemicals mediated by the presence of DOC in soils and other porous media has been documented by a number of studies [*McCarthy and Zachara*, 1989]. In these studies, it is generally assumed that DOC is a non-reactive component of the aqueous phase with respect to interactions with bulk soil material (BSM). However, there is evidence that also the carrier DOC itself undergoes adsorption to the soil matrix [*David and Vance*, 1991; *Jardine et al.*, 1990].

The development of simulation models for describing the fate of HOC in soils has gained increasing popularity in recent years. The fate of a particular contaminant under a unique combination of environmental conditions can best be estimated by simultaneously considering all important processes and integrating them through a modeling approach. A three phase system [*McCarthy and Zachara*, 1989] accounts for the distribution between the aqueous phase, the bulk soil and the mobile sorbent, which can be considered as a third phase or pseudophase [*Edwards et al.*, 1991].

For the modeling and simulation of carrier influenced transport of HOC a comprehensive approach has to take into account nonlinear rate functions and isotherms.

This paper will focus on the modeling and simulation of DOC influenced transport of HOC allowing for a system of sorption processes which are in equilibrium or nonequilibrium, except for the sorption of HOC to DOC, which has to be an equilibrium reaction. The model proposed allows for both nonlinear isotherms and rate functions. This means that the transport of HOC and of carrier DOC has to be formulated in a multicomponent approach. The reaction pathways considered are

- sorption of HOC to BSM
- sorption of DOC to BSM
- formation of HOC-DOC compounds
- sorption of HOC-DOC to BSM.

The work of *Karickhoff* [1980], *Maxin* [1992] and others shows, that the sorption of HOC to the BSM can be kinetically controlled, whereas the partition of HOC between water and DOC can be considered as an equilibrium process. However, the sorption isotherm for the sorption of HOC to the BSM and to DOC can be nonlinear.

# THE MODEL

The proposed model (Fig.1) is developed for the simulation of the reactive carrier influenced transport of reactive HOC through porous media. It considers both equilibrium and nonequilibrium sorption of the HOC to the bulk soil material. The presence of dissolved organic carbon as a mobile sorbent leads to the formation of

'complex-like' colloids build of DOC and HOC. The formation of the carrier bound HOC reduces the mass concentration of free solute HOC. Thus, both the sorbed and the dissolved concentration of HOC will be affected. The model considers further the sorption of the carrier-bound HOC to the bulk soil material (Fig. 2). Analogous to the sorption of free HOC, the model states two possible mechanisms for the sorption of the carrier-bound HOC: instantaneous equilibrium sorption sites and kinetically controlled nonequilibrium sorption sites. This conceptual approach results in a fractionation of the BSM into different sorption sites referring to the corresponding processes and involved chemical species (Fig. 3):

Type $\Psi_{Hf}$: equilibrium sorption sites for free HOC

Type $\varphi_{Hf}$: nonequilibrium sorption sites for free HOC

Type $\Psi_{Hb}$: equilibrium sorption sites for carrier-bound HOC

Type $\varphi_{Hb}$: nonequilibrium sorption sites for carrier-bound HOC

For an explanation of the abbreviations and for a complete list of notation see Appendix A. In the following we denote the fraction of the bulk density with $\rho_\alpha$ for the type $\alpha$. We also take into account the equilibrium and nonequilibrium sorption of the carrier DOC (Fig .2), such that DOC appears in exactly the same forms as HOC and analogous collections of sorption sites can be attributed:

Type $\Psi_{Df}$: equilibrium sorption sites for free DOC

Type $\varphi_{Df}$: nonequilibrium sorption sites for free DOC

Additionally, if we consider the HOC-DOC compound from the viewpoint of total DOC, also types $\Psi_{Db}$ and $\varphi_{Db}$ appear, which are identical with $\Psi_{Hb}$ and $\varphi_{Hb}$. Reasonable relations between the different collections of sorption sites will be discussed in the section on *effective isotherms and rate functions.*

The knowledge about the sorption process mentioned and in particular about the formation of the HOC-DOC compounds is still scarce. At present, reaction mechanisms and stoichiometry of reactions involving HOC and naturally occuring DOC are essentially unknown. Only recently laboratory batch experiments have been performed leading to sorption isotherms and rate function description.

Therefore we have to use this type of information in the formulation of the model, in particular we have to use mass concentrations instead of molar concentrations. Often only the total DOC concentration is accessible experimentally. We use it as a reference to describe the formation of the HOC-DOC compounds in terms of an isotherm. For this process we neglect kinetic effects. This is in accordance with experimental findings [*Maxin,* 1992, *McCarthy and Jimenez,* 1985], but also sets the basis for a transformation of the model. This transformed model is considerably simpler than the

original formulation. In this way we are able to set up a model which only uses information on a two phase system, but is capable to make quantitative statements about the overall chemistry in terms of *effective isotherms and effective rate functions* and also shows the interplay of chemistry and transport.

*Mathematical formulation*

The conservation of mass for a substance in solution reads:

$$\partial_t(\theta C)(x,t) = -\mathrm{div}(J(x,t)) + P(x,t) \qquad (1)$$

where $\partial_t$ denotes differentiation with respect to time, $\theta$ $[L^3/L^3]$ the volumetric water content with respect to unit volume of porous medium, C $[M/L^3]$ the mass concentration of solute related to the part of a representative elementary volume (REV) filled with water, J the volumetric flux $[M/L^2/T]$, P the volumetric consumption or production rate $[M/L^3/T]$ (i.e. due to adsorption), $\mathrm{div}(\cdot)$ the divergence operator, x and t the variables of space and time [L], [T] respectively. The following discussion holds true independent of the spatial dimension. For the general discussions one may think of laboratory (soil column) or field situations, with saturated or partially unsaturated, stationary or instationary flow regime. Due to the tracer situations the quantities related to the flow regime are assumed to be independent of the concentrations of the chemicals. We restrict our discussions to the case were only sorption acts as a sink or a source. For easier comprehension chemical, photochemical or biological degradation will not be considered here although these processes might be incorporated without difficulties. This assumption is valid for extremly hydrophobic organic chemicals, such as PAHs or PCBs.
The volumetric mass flux J is the sum of the advectice flux and the dispersive and diffussive fluxes.

This means

$$J = -\theta D \nabla C + q \cdot C \qquad (2)$$

where $D[L^2/T]$ is the sum of the molecular diffusion and the mechanical dispersion matrix and q [L/T] the specific discharge.
Combining equations (1) and (2) leads to the well known advection-dispersion equation (ADE)

$$L(C) := \partial_t(\theta C) - \mathrm{div}(\theta D \nabla C - qC) = P \qquad (3)$$

i. e. we use L(C) to abbreviate the linear part of the differential operator ($L(C)=0$ describes inert transport).
We will now elucidate the term P, which represents the sources or/and sinks. The chemical processes to be considered are nonlinear equilibrium and nonequilibrium

sorption reactions. As shown in the conceptual derivation of the model, this leads to a subdivision of the BSM in distinct fractions which perform different chemical sorption processes. Thus we get for the source/sink P(X,T)

$$P(x,t) = -\rho_{eq} \cdot \partial_t \Psi(C(x,t)) - \rho_{neq} \cdot \partial_t S(x,t) \qquad (4)$$

where $\rho_{eq}$ and $\rho_{neq}$ are the bulk density of fractions of the BSM assigned to equilibrium or nonequilibrium sites respectively, $\Psi(C(x,t))$ [M/M] and S [M/M] denotes the mass concentration related to the chemical sorbed to equilibrium or nonequilibrium sites, respectively.
In the following, a mass concentration $C_\alpha$ is always defined relative to the water filled part of an REV, whereas mass concentrations $\Psi_\alpha$ or $S_\alpha$ are defined related to the part of mass of porous skeleton attributed to sorption sites of type $\psi\alpha$ or $\varphi\alpha$, respectively.
For the transport of HOC through a porous medium there exist two possible transport pathways: the advective-dispersive flow of the free (solute) HOC $C_{Hf}$ and the advective-dispersive transport of the carrier-bound HOC $C_{Hb}$. Combining equations (3) and (4) to describe the reactive transport of the HOC and identifying the adequate fractions of the BSM the transport of free HOC is described by

$$\partial_t(\theta C_{Hf}) + \rho_{\Psi Hf}\, \partial_t \Psi_{Hf}(C_{Hf}) + \rho_{\varphi Hf} \cdot \partial_t S_{Hf} - \\ -\mathrm{div}(\theta D \nabla C_{Hf} - q C_{Hf}) = F \qquad (5a)$$

where $\rho_{\Psi Hf}$ and $\rho_{\varphi Hf}$ denote the bulk density of the fraction of the BSM providing equilibrium sorption sites and nonequilibrium sorption sites for the free HOC, $C_{Hf}$ the mass concentration of free HOC in liquid phase, $\Psi_{Hf}$ the mass concentration of free HOC sorbed to the fraction of BSM providing equilibrium sorption sites, $S_{Hf}$ the mass concentration of free HOC sorbed to the fraction of BSM providing nonequilibrium sorption sites and F the rate of loss of free HOC due to the formation of carrier-bound HOC.
Analogous to the transport of free HOC we find for the carrier-bound HOC the following equation

$$\partial_t(\theta C_{Hb}) + \rho_{\Psi Hb}\, \partial_t \Psi_{Hb}(C_{Hb}) + \rho_{\varphi Hb} \cdot \partial_t S_{Hb} - \\ - \mathrm{div}(\theta D \nabla C_{Hb} - q C_{Hb}) = - F \qquad (5b)$$

where $\rho_{\Psi Hb}$ and $\rho_{\varphi Hb}$ denote the bulk density of the fraction of the BSM providing equilibrium sorption sites and nonequilibrium sorption sites for the carrier-bound HOC, $C_{Hb}$ the mass concentration of carrier-bound HOC in liquid phase, $\Psi_{Hb}$ the mass concentration of carrier-bound HOC sorbed to the fraction of BSM providing equilibrium sorption sites for carrier-bound HOC, $S_{Hb}$ the mass concentration of carrier-bound HOC sorbed to the fraction of BSM providing nonequilibrium sorption sites to carrier-bound HOC and -F is the rate of gain of carrier-bound HOC due to

the formation of carrier-bound HOC.
More precisely $C_{Hb}$ measures the mass fraction of HOC of the HOC-DOC compound related to the water filled part of an REV. With respect to the formation of the HOC-DOC compounds this concept allows us to identify the gain rate in terms of the loss rate for the free HOC without knowledge on the chemical nature of the reaction. One may argue, that information related to $C_{Hb}$, i.e. the sorption isotherm $\Psi_{Hb}(C_{Hb})$, is not accessible experimentally. We will discuss this point in the section on the *transformed model*. Implicit in the formulation (5a,b) is the assumption that the association of different compounds in fact can be described as sorption process, i.e. without taking competition of other compounds into account. Again we discuss this point in the section on the *transformed model*. The choice of this formulation is mainly due to the available experimental information, the mathematical procedure could also be persued for some general concept, like e.g 'competitive' isotherms (see the section on *extensions and numerical approximations*). As the HOC-DOC compounds usually have a huge particle size compared to the HOC particles, one may expect that only a small part of the pore space is accessible to the HOC-DOC particles leading to a pore size exclusion effect. This would result in a different water content $\theta_1$ and $\theta_2$, with $\theta_2 \leq \theta_1$, in equation (5a) and (5b). An extension of the following considerations is possible (see the section on *extensions and numerical approximations*).
The kinetics of the nonequilibrium adsorption wil be described in a general fashion by

$$\partial_t S_{Hf} = g_{Hf}(C_{Hf}, S_{Hf}) \tag{6a}$$

for the case of sorption of free HOC and

$$\partial_t S_{Hb} = g_{Hb}(C_{Hb}, S_{Hb}) \tag{6b}$$

for the case of carrier-bound HOC. The properties of the rate functions $g_{Hf}$ and $g_{Hb}$ will be discussed in detail later.
The system (5a,b) and (6a,b) has to be supplemented with appropriate boundary and initial conditions. As the usual choices provide no problems in the following transformations, we will not do this explicitly.

## THE TRANSFORMED MODEL: EFFECTIVE ISOTHERMS AND RATE FUNCTIONS

The equations still contain the unspecified term F. Our objective is to transform the model such that F does not appear explicitly anymore. We choose the total mass concentration $C_H$

$$C_H := C_{Hf} + C_{Hb} \tag{7}$$

as a new variable.

By adding (5a) and (5b), the governing transport equation for the total mass concentration of HOC in the liquid phase then becomes

$$\partial_t(\theta C_H)+\rho_{\Psi Hf}\cdot\partial_t\Psi_{Hf}(C_{Hf})+\rho_{\varphi Hf}\cdot\partial_t S_{Hf}+\rho_{\Psi Hb}\cdot\partial_t\Psi_{Hb}(C_{Hb})+$$
$$\rho_{\Psi Hb}\cdot\partial_t S_{Hb}-\mathrm{div}(\theta D\nabla C_H - qC_H)=0 \qquad (8)$$

Equation (8) in combination with (6a) and (6b) represent the overall transport of reactive chemicals through porous media in the presence of reactive carriers. It will further be referred to as the *general statement of the transport model*. The aim of the following transformations is to derive a formulation for the relation of the partial mass concentrations $C_{Hf}$ and $C_{Hb}$ on the total mass concentration $C_H$ of the HOC in the liquid phase. The advantages are obvious: for analytical reasons we are not able to determine the partial concentrations but the total concentration of the HOC in liquid phase. So the appropriate formulation will be the formulation in terms of overall concentrations of HOC and carrier DOC.
For the further discussions we assume that the formation of carrier-bound HOC is an equilibrium reaction, which means that the association of HOC and DOC is rapid compared to the mean pore water velocity in the porous medium. Analytical data obtained in batch kinetic experiments support the validity of this assumption [*McCarthy and Jimenez,* 1985, *Maxin,* 1992]. The mass concentration of carrier-bound HOC, $C_{Hb}$, can than be expressed in terms of the mass concentration of total DOC present in liquid phase, $C_D$, and the 'sorption- isotherm' of HOC sorption to the carrier molecule DOC, $\Pi(C_{Hf})$:

$$C_{Hb} = C_D \cdot \Pi(C_{Hf}) \qquad (9)$$

Here we refer to the total concentration of DOC both due to experimental restrictions and due to a desired partial decoupling of the problem: Obviously, the presence of DOC influences the dynamics of HOC, but we want to have the dynamics of the appearing DOC concentration to be independent of the HOC concentrations.
Substituting equation (9) in (7) we get for the total mass concentration of HOC $C_H$ present in liquid phase

$$C_H = C_{Hf} + C_D\Pi(C_{Hf}) \qquad (10)$$

Now we can express the mass concentration of free HOC and carrier-bound HOC in liquid phase, $C_{Hf}$ and $C_{Hb}$, as a function of the total mass concentration of HOC and the total mass concentration of DOC in liquid phase:

$$C_{Hf} = G(C_D, C_H) \qquad (11a)$$

$$C_{Hb} = C_H - G(C_D, C_H) = C_D\Pi(G(C_D,C_H)) \qquad (11b)$$

where $G(C_D, C_H)$ denotes the implicit expression of the dependency of the mass concentration of free HOC on the mass concentration of DOC and the total mass concentration of HOC given by (10).
This unique resolution exists under minimal assumptions on $\Pi$, e.g. monotonicity of $\Pi$, but in general no explicit formula is available.
With this, both the equilibrium sorption of free HOC and carrier-bound HOC can be expressed as a function of the total mass concentration of HOC and DOC present in liquid phase

$$\Psi(x,t,C_H) := \rho_{\Psi Hf}/\rho_{\Psi H} \cdot \Psi_{Hf}(G(C_D(x,t),C_H)) + \\ + \rho_{\Psi Hb}/\rho_{\Psi H} \cdot \Psi_{Hb}(C_H - G(C_D(x,t), C_H)) \tag{12}$$

where $\Psi(x,t,C_H)$ denotes the total mass concentration of HOC composed of free and carrier-bound HOC sorbed to sorption sites of the BSM providing equilibrium sorption sites, and $\rho_{\Psi H}$ the bulk density of the fraction of BSM providing equilibrium sorption sites both for the free and the carrier-bound HOC.
Equation (12) represents the overall sorption of HOC due to the sorption of free HOC and carrier-bound HOC to equilibrium sorption sites and is called the *effective isotherm*. The properties of the effective isotherm will be discussed in a subsequent section of this paper.
With Eq. (12) the general transport model can be expressed in an equivalent form in terms of the effective isotherm:

$$\partial_t(\theta C_H) + \rho_{\Psi H}\, \partial_t\Psi(x,t,C_H) + \rho_{\varphi Hf} \cdot \partial_t S_{Hf} \\ + \rho_{\varphi Hb} \cdot \partial_t S_{Hb} - \mathrm{div}(\theta D \nabla C_H - qC_H) = 0 \tag{13a}$$

and

$$\partial_t S_{Hf} = f_{Hf}(x,t,C_H,S_{Hf}) \tag{13b}$$

where

$$f_{Hf}(x,t,C,S) := g_{Hf}(G(C_D(x,t),C), S)$$

for the case of sorption of free HOC and

$$\partial_t S_{Hb} = f_{Hb}(x,t,C_H,S_{Hb}) \tag{13c}$$

where

$$f_{Hb}(x,t,C,S) := g_{Hb}(C - G(C_D(x,t), C), S)$$

$f_{Hf}$ and $f_{Hb}$ are called *effective rate functions.*
The formulation (13) is feasable to study the interplay of the different sorption processes and of transport and the influence of the total DOC concentration $C_D$. The model for the dynamics of $C_D$ still has to be set up. In particular, to restrict the complexity of the model, it should be independent of $C_H$. We persue this point in the next section. The model (13) resembles the form of the well known one component equilibrium and nonequilibrium multiple site adsorption model (with three different types of sites). The distinction is the dependence of the isotherm and the rate functions on the concentration $C_D$ and in this way possibly on space and time. In the section on the properties of the effective isotherm we indicate possible implications.
As we will encounter this situation in the next subsection, we note that the transformation is also possible if the original isotherm and rate functions depend on $C_D$ or x,t.

*Possible scenarios*

In the following we consider two possible scenarios and point out conditions under which we can describe both the sorption process as postulated in (5a,b;6a,b) and have a description of the DOC dynamics independent of the HOC concentrations. In this case we consider only a well-defined fraction (e.g hydrophobic acids according to the fractionation scheme of *Leenheer* [1981]) of the DOC in the sense that each HOC-DOC particle consists of the same amount of mass of DOC and of mass of HOC. Let $\alpha$ denote the corresponding quotient, then

$$C_{Db} = \alpha C_{Hb} = \alpha C_D \Pi(C_{Hf}) \qquad (14)$$

$$S_{Db} = \alpha S_{Hb},$$

where the index Db refers to the mass fraction of DOC of the HOC-DOC colloids.

We consider the *s*cenario A:
With respect to sorption free HOC, the HOC-DOC colloids, and free DOC act as different species, in particular the collections of sorption sites are pairwise disjoint.
Then the justification of the equations (5,6) is clear, but in general the description of $C_D$ depends on $C_{Hf}$. In the following we use a notation analogous to the different fractions of HOC with H in the index substituted by D. Following the procedure applied for HOC we arrive at the following equations for

$$C_D = C_{Df} + C_{Db} \tag{15}$$

we find

$$\begin{aligned} &\rho_{\Psi Df}\, \partial_t \Psi_{Df}(C_{Df}) + \rho_{\Psi Db} \partial_t \Psi_{Db}(C_{Db}) + \\ &\quad + \rho_{\varphi Df}\, \partial_t S_{Df} + \rho_{\varphi Db}\, \partial_t S_{Db} + L(C_D) = 0 \\ &\partial_t S_{Df} = g_{Df}(C_{Df}, S_{Df}) \\ &\partial_t S_{Db} = g_{Db}(C_{Db}, S_{Db}). \end{aligned} \tag{16}$$

and by (14)

$$\begin{aligned} C_{Db} &= \alpha \Pi(C_{Hf}) C_D, \\ C_{Df} &= (1 - \alpha \Pi(C_{Hf})) C_D \end{aligned} \tag{17}$$

By neglecting $C_{Db}$ ( and $S_{Db}$) we can avoid the dependence on $C_{Hf}$. Such an assumption seems to be doubtful, even if $C_H$ is several orders of magnitude smaller than $C_{Df}$, as we expect $\alpha$ to be very large.
Nevertheless, in the case of linear isotherms and rate functions, being the same for free and carrier-bound HOC, equations (16) reduce to a linear problem for $C_D$ and $S_D$ (defined in (19)), independent of $C_{Hf}$: Let

$$\begin{aligned} &\rho_{\Psi Df}/\rho_{\Psi D} \cdot \Psi_{Df}(C) = KC \\ &\rho_{\Psi Db}/\rho_{\Psi D} \cdot \Psi_{Db}(C) = KC \\ &\rho_{\varphi Df}/\rho_{\varphi D} \cdot g_{Df}(C,S) = k_a C - k_d\, \rho_{\varphi Df}/\rho_{\varphi D} \cdot S \\ &\rho_{\varphi Db}/\rho_{\varphi D} \cdot g_{Df}(C,S) = k_a C - k_d\, \rho_{\varphi Db}/\rho_{\varphi D} \cdot S \end{aligned} \tag{18}$$

$K$, $k_a$, $k_d > 0$ are constants, $\rho_{\Psi D}$, $\rho_{\varphi D}$ are e.g. the fractions of bulk density related to equilibrium and nonequilibrium sorption sites for DOC. Then

$$\rho_{\Psi D}\,\partial_t(KC_D) + \rho_{\varphi D}\partial_t S_D + L(C_D) = 0$$
$$\partial_t S_D = k_a C_D - k_d S_D, \tag{19}$$

where

$$S_D := \rho_{\varphi Df}/\rho_{\varphi D} \cdot S_{Df} + \rho_{\varphi Db}/\rho_{\varphi D} \cdot S_{Db}.$$

The *scenario B* reads:
With respect to sorption free DOC and the HOC-DOC compounds are indistinguishable, but they act as different species compared to HOC, in particular the first collections of sorption sites are the same and disjoint from the last one.
Then it is clear that for the total concentration of DOC equations of the following type hold true:

$$\rho_{\Psi D}\,\partial_t\Psi_D(C_D) + \rho_{\varphi D}\partial_t S_D + L(C_D) = 0,$$
$$\partial_t S_D = g_D(C_D, S_D). \tag{20}$$

The problem lies here in the justification of $\Psi_{Hb}$ and $g_{Hb}$: Because of (14) the fraction of the total DOC in solution in form of HOC-DOC compounds is $\alpha\Pi(C_{Hf})$, and thus also in the sorbed phase related to equilibrium sorption sites, i. e. with reference to the collections of equilibrium sorption sites of DOC the sorbed mass concentration is $\alpha\Pi(C_{Hf})\Psi_D(C_D)$.
By (14) this means for HOC in form of HOC-DOC compounds

$$\rho_{\Psi Hb}\Psi_{Hb} = \rho_{\Psi D}\,\Psi_D(C_D)/C_D \cdot C_{Hb}, \tag{21}$$

where $\Psi_{Hb}$ denotes the sorbed mass concentration of bound HOC related to the mass fraction containing the equilibrium sorption sites. Thus (21) defines a generalized isotherm analogous to (12), as $\Psi_{Hb} = \Psi_{Hb}\,(x,t,C_{Hb})$ is linear in $C_{Hb}$, but x,t-dependent by means of its $C_D$ dependence.
For the nonequilibrium sorption reaction we cannot argue in the same way, as due to the time dependence of $C_{Hf}$ we cannot expect the fraction of the total DOC in form of HOC-DOC compounds to be $\alpha\Pi(C_{Hf})S_D$. For the special case of a linear rate function, i.e.

$$\partial_t S_D = k_a C_D - k_d S_D \tag{22}$$

for constants $k_a$, $k_d$, by means of (14) $C_D$ can be splitted in $C_{Df}$ and $C_{Db}$ and thus also $S_D$ (compare (18)):

$$S_D = \rho_{\varphi Df}/\rho_{\varphi D} \cdot S_{Df} + \rho_{\varphi Db}/\rho_{\varphi D} \cdot S_{Db} \tag{23}$$

fulfilling equation (22) and with the appropriate meaning provided the same holds already true for t=0. This can be expressed by the conditions

$$S_{Df}(0)/S_{Db}(0) = (1-\alpha\Pi(C_{Hf}(0)))/(\alpha\Pi(C_{Hf}(0))) \; \rho_{\varphi Db}/\rho_{\varphi Df} \tag{24}$$

Then by (14) also $S_{Hb}$ is well defined and fulfills equation (22).

## SPECIAL CASES

In this section we will discuss how to apply the model for special cases as for example batch sorptions experiments or some model statement presented in recently published papers dealing with transport modeling of reactive solute chemicals.

*A: linear sorption of HOC to carrier DOC*

Assume that the partition of HOC between carrier DOC and liquid phase is a linear function of the total mass concentration of HOC in the liquid phase, that is

$$\Pi(C_{Hf}) := K_{HD} \cdot C_{Hf} \tag{25}$$

where $K_{HD}$ denotes the partition coefficient of HOC between carrier DOC and liquid phase. This assumption seems to be valid for the case when the concentration of HOC is very small compared to the concentration of carrier DOC. This situation is usually met in surface and subsurface horizons of soils. Then $C_{Hb}$, the concentration of carrier-bound HOC can be written as

$$C_{Hb} := C_D \cdot K_{HD} \cdot C_{Hf} \tag{26}$$

With that, $G(C_D, C_H)$ is of explicit type:

$$G(C_D, C_H) := 1 / (1+C_D \cdot K_{HD}) \cdot C_H \tag{27},$$

and we get for the effective isotherm $\Psi(x,t,C_H)$

$$\begin{aligned}\Psi(x,t,C_H) := {} & \rho_{\Psi Hf}/\rho_{\Psi H} \cdot \Psi_{Hf}(1/(1+C_D(x,t) \cdot K_{HD}) \cdot C_H) + \\ & + \rho_{\Psi Hb}/\rho_{\Psi H} \cdot \Psi_{Hb}(C_D(x,t) \cdot K_{HD}/(1+C_D(x,t) \cdot K_{HD}) \cdot C_H)\end{aligned} \tag{28}$$

If we further assume that $\Psi_{Hf}$ and $\Psi_{Hb}$, the sorption isotherms of the free HOC and

the carrier-bound HOC, respectively, are also linear sorption isotherms:

$$\Psi_{Hf} := K_{Hf} \cdot C_{Hf} \tag{29a}$$

$$\Psi_{Hb} := K_{Hb} \cdot C_{Hb} \tag{29b}$$

where $K_{Hf}$ and $K_{Hb}$ denote the partition coefficient for the free and the carrier bound HOC, respectively, the effective isotherm is of complete explicit type and can be determined analytically by computing

$$\begin{aligned}\Psi(x,t,C_H) := {} & \rho_{\Psi Hf}/\rho_{\Psi H} \cdot 1/(1+C_D(x,t) \cdot K_{HD}) \cdot K_{Hf} \cdot C_H + \\ & + \rho_{\Psi Hb}/\rho_{\Psi H} \cdot C_D(x,t) \cdot K_{HD}/(1+C_D(x,t) \cdot K_{HD}) \cdot K_{Hb} C_H\end{aligned} \tag{30}$$

Under the restriction of no sorption of carrier-bound HOC to the bulk soil material, that means $K_{Hb} \equiv 0$, the effective isotherm reduces to

$$\Psi(x,t,C_H) := \rho_{\Psi Hf}/\rho_{\Psi H} \cdot 1/(1+C_D(x,t) \cdot K_{HD}) \cdot K_{Hf} \cdot C_H \tag{31}$$

This is the form of the effective isotherm used by *Kan* and *Tomson* [1989], *Dunnivant et al.* [1992a] and *Mageo et al.* [1991]. The application of the model with such restrictions is limited to the case of non-reactive carrier influenced transport of reactive solutes. The demands for the simulation of reactive carrier influenced transport are not met by this type of model. One should note that in the case of DOC as carrier molecule, the sorption and desorption of DOC has to be taken into account and that the assumption of DOC being a non-reactive carrier is no longer valid for the case of carrier influenced transport of solutes through natural soils [*Jardine et al.*, 1989].
*Lafrance et al.* [1989] suggested a three site transport model for reactive chemicals in porous media, which can also be considered as a special case of the general model if the following assumptions made by the authors are introduced. These assumptions are two types of sorption sites, one instantaneous, which should be describable by non-linear Freundlich type sorption isotherms and nonequilibrium sorption sites, accessible to the free dissolved chemical. A third nonequilibrium site should be accessible to the complexed (carrier-bound) chemical.
They restrict their discussions to the case, where only monovalent complexation reactions are involved in the formation of carrier-bound chemicals. This corresponds to a description like (9) with linear $\Pi$. Little is known on the chemical and structural properties of DOC as a carrier molecule in soils. Consequently we consider the restriction to only monovalent complexation reactions as too strict. If we think of the DOC as spherical huge macromolecules one can imagine that the generally much smaller HOC can be incorporated in the interior of the DOC macromolecule. Another possible pathway could be the formation of micelle-like structures as described by *Wershaw* [1986].
Experimental data show the significant affinity of DOC to BSM [*Jardine et al.* , 1989,

*David and Vance,* 1991, *Dunnivant et al.,* 1992b]. This means, that the assumption of DOC being a non-reactive chemical is no longer valid. Consequently the assumption, that the sorption of carrier-bound HOC is much greater compared to the sorption of carrier DOC alone does not seem to meet with the natural situation. This assumption holds for the case in which the sorption of the carrier-bound molecule is due to a specific sorption mechanism, which depends on a funtional group of the reactive chemical. In general, we can not exclude non-specific sorption mechanisms and therefore a model for carrier facilitated transport should take into account the sorption of the carrier molecules itself.
*Enfield et al.* [1989] developed a different approach to simulate the influence of macromolecules on reactive chemical transport. Their fundamental assumption is that the solute carrier macromolecule does not undergo sorption reactions itself. They divide the total flow domain in two subdomains governed by two distinct 'mobile phases: a mobile aqueous phase and a mobile organic phase. Each phase is assigned an own flow regime which is characterized by different dispersion coefficients and mean pore water velocities. For each domain they applied an advection-dispersion equation to describe the transport of the two mobile phases. The transfer between the mobile phases is described by rate functions acting as sinks for one phase and as source for the other phase. The interaction between mobile phases and immobile solid phases is described by rate functions, too. All rate functions are assumed to be of first order, i.e. linear type.
The conceptual division of the flow domain into a mobile organic and a mobile aqueous phase seems to be appropriate to simulate carrier facilitated transport. But one has to note, that there actually is no organic liquid phase with intrinsic mobility present (as for example oil). The mobility of the organic macromolecules depends on their dissolution in the aqueous phase. So the proposed division of the flow domain is a pragmatic way of describing the transport phenomena observed in porous media.
In contrast, a mechanistic approach to describe the fact that a part of the porous medium is not accessible to the mobile phase would be to consider the exclusion of smaller pores for the dissolved macromolecules. We will discuss the consequenc for the general model in the section on *extensions and numerical approximations.*

*B Batch experiments: equilibrium sorption isotherms and kinetics*

The fundamental property of batch experiments is their homogeneity in space. So $C_H$, $S_{Hf}$, $S_{Hb}$ are independent of space and

$$\mathrm{div}(\theta D \nabla C_H - qC_H) \equiv 0.$$

with that (13a) reduces to

$$\partial_t(\theta C_H)+\rho_{\Psi H}\cdot\partial_t\Psi(t,C_H)+\rho_{\varphi Hf}\cdot\partial_t S_{Hf}+\rho_{\varphi Hb}\cdot\partial_t S_{Hb}=0$$

or (32a)

$$\theta\cdot C_H+\rho_{\Psi H}\cdot\Psi(t,C_H)+\rho_{\varphi Hf}\cdot S_{Hf}+\rho_{\varphi Hb}\cdot S_{Hb} \text{ is constant.}$$

The rate functions for the sorption to nonequilibrium sites will be

$$\partial_t S_{Hf} = g_{Hf}(t, C_H, S_{Hf}) \tag{32b}$$

$$\partial_t S_{Hb} = g_{Hb}(t, C_H, S_{Hb}) \tag{32c}$$

The equations for $C_D$, e.g. (20), simplify analogously.
Batch experiments are an appropriate method to determine capacity and kinetics of the sorption of HOC to BSM in the absence and presence of carrier DOC. These experiments can be used to determine the adequate sorption isotherm or the rate functions g.
Equations (32a,b,c) are the statement of the general model in the batch experiment case. The problem is to solve the ordinary differential equations (32a,b,c) for known initial values at the initial time, say t=0.

$$C_H(0) = C_{H0};\ S_{Hf}(0) = S_{Hf0};\ S_{Hb}(0) = S_{Hb0}.$$

*Kinetic rate functions*

If we are interested in the kinetics of the sorption process, we have to integrate equation (32a) for distinct times t≠0 over the intervall [0,t]. The conservation of mass then leads for every distinct time t to the problem

$$\theta \cdot C_H + \rho_{\Psi H} \cdot \Psi(t,C_H) + \rho_{\varphi Hf} \cdot S_{Hf} + \rho_{\varphi Hb} \cdot S_{Hb} = \theta \cdot C_{H0} + \rho_{\Psi H} \cdot \Psi(0,C_{H0}) + \rho_{\varphi Hf} \cdot S_{Hf0} + \rho_{\varphi Hb} \cdot S_{Hb0} \tag{33a}$$

$$\partial_t S_{Hf} = f_{Hf}(t, C_H, S_{Hf}) \tag{33b}$$

$$\partial_t S_{Hb} = f_{Hb}(t, C_H, S_{Hb}) \tag{33c}.$$

*Equilibrium sorption isotherms*

If we are interested in the equilibrium sorption isotherms, we have to solve the equations (33a,b,c) for the time $t \to \infty$. We expect the stabilization

$$C_H(t) \rightarrow C_H^{eq}$$

$$S_{Hf}(t,C_H) \rightarrow S_{Hf}^{eq}$$

$$S_{Hb}(t,C_H) \rightarrow S_{Hb}^{eq}$$

$$C_D(t) \rightarrow C_D^{eq}$$

The rate functions for the sorption of the free HOC and the carrier-bound HOC to the nonequilibrium sites are zero. Usually, the sorbed concentrations are only functions of the dissolved total concentration of HOC(compare (36)-(38)):

$$\begin{aligned} f_{Hf}(\infty, C_H, S_{Hf}) = 0 \Longleftrightarrow S_{Hf} = S_{Hf}^{eq}(C_H) \\ f_{Hb}(\infty, C_H, S_{Hb}) = 0 \Longleftrightarrow S_{Hb} = S_{Hb}^{eq}(C_H). \end{aligned} \tag{34}$$

Here $f_{Hf}(\infty, C, S)$ is given by (13b) and $C_D = C_D^{eq}$ and $f_{Hb}(\infty, C, S)$ in an analogous way by (13c).
Equation (33a) implies

$$\begin{aligned} &\theta C_H^{eq} + \rho_{\Psi H}\,\Psi(C_H^{eq}) + \rho_{\varphi Hf} \cdot S_{Hf}^{eq}(C_H^{eq}) + \rho_{\varphi Hb} \cdot S_{Hb}^{eq}(C_H^{eq}) = \\ &= \theta C_{H0} + \rho_{\Psi H} \cdot \Psi(C_{H0}) + \rho_{\varphi Hf} \cdot S_{Hf0} + \rho_{\varphi Hb} \cdot S_{Hb0} = \\ &= \theta \cdot C_H^i \end{aligned} \tag{35}$$

where $(\theta C_H^i)$ is the total mass concentration of HOC added to the system at time $t=0$. The superscript eq denotes equilibrium.
For given $C_H^i$ equation (35) is a nonlinear equation for $C_H^{eq}$, or if equations (34) can not be resolved explicitly, equations (34), (35) are (nonlinear) equations for $C_H^{eq}$, $S_{Hf}^{eq}$, $S_{Hb}^{eq}$. They can be resolved numerically.

## PROPERTIES OF THE EFFECTIVE ISOTHERM AND RATE FUNCTIONS

Our aim is to discuss the properties of effective isotherms and rate functions starting from general, i.e. in particular nonlinear isotherms $\Psi_{Hf}$, $\Psi_{Hb}$, $\Pi$ and rate functions $g_{hf}$, $g_{Hb}$ in the original formulation (5), (6) and (9). To make our reasoning correct, several properties of $\Psi_{Hf}$ etc are neccessary, which will be introduced lateron and are fulfilled by all commonly used isotherms and rate functions (see e.g. *van Duijn and Knabner*, 1992a). In particular we can allow for the Freundlich isotherm with exponent less than 1.

Concerning the nonequilibrium reactions, we assume that the corresponding equilibria are given by isotherms, i.e there are functions $\varphi_{Hf}$, $\varphi_{Hb}$ such that

$$g_{Hf}(C_{Hf}, S_{Hf}) = 0 \Longleftrightarrow S_{Hf} = \varphi_{Hf}(C_{Hf})$$

$$g_{Hb}(C_{Hb}, S_{Hb}) = 0 \Longleftrightarrow S_{Hb} = \varphi_{Hb}(C_{Hb}) \tag{36}$$

Obviously this is the case if one uses the following explicit form:

$$g_{Hf}(C_{Hf}, S_{Hf}) = k_{Hf}(\varphi_{Hf}(C_{Hf}) - S_{Hf}) \tag{37}$$

with a rate parameter $k_{Hf} > 0$, and analogously for $g_{Hb}$.
The effective rate functions $f_{Hf}$, $f_{Hb}$ preserve the property (36) with the following isotherms

$$f_{Hf}(x,t,C_H,S_H) = 0 \Longleftrightarrow$$

$$S_H = \chi_{Hf}(x,t,C_H) := \varphi_{Hf}(G(C_D(x,t),C_H)$$

$$f_{Hb}(x,t,C_H,S_H) = 0 \Longleftrightarrow \tag{38}$$

$$S_H = \chi_{Hb}(x,t,C_H) := \varphi_{Hb}(C_H - G(C_D(x,t),C_H)$$

Futhermore also the explicit form (37) is preserved with the isotherm defined in (38). We observe that the isotherms $\chi_{Hf}$, $\chi_{Hb}$ have the same structure as the constituents of the effective isotherm $\Psi$ (defined in (12)) describing the equilibrium adsorption process. This means that we can restrict the following discussion to the equilibrium adsorption process: Due to (38) the nonequilibrium process will have the same properties discussed below, modified by the delays of a nonequilibrium process.
Therefore we now turn to the properties of the effective isotherm. We assume that

$$\Pi(0) = 0,\ \Pi(C) > 0 \text{ for } C > 0,$$

$$\Pi'(C) \geq 0 \text{ for } C = 0 \tag{39}$$

$$(\Pi'(0) = \infty \text{ is allowed})$$

and the same properties for $\Psi_{Hf}$, $\Psi_{Hb}$. Here $\cdot'$ denotes the derivative. If a function depends on several variables, we will write the differential explicitly.
First we look at the limit case of the model: For $C_D(x,t) \to 0$ (for fixed (x,t) and $C_H(x,t)$) we expect the model to reduce to the adsorption model only dealing with sorption to the soil. In fact, then by (10)

$$C_{Hf}(x,t) \rightarrow C_H(x,t)$$

and thus $C_{Hb}(x,t) \rightarrow 0$, i.e.

$$\Psi(x,t,C_H(x,t)) \rightarrow \rho_{\Psi Hf}/\rho_{\Psi H}\ \Psi_{Hf}(C_H(x,t)) \tag{40}$$

Thus locally at (x,t) there is no reduction in sorption of $C_{Hf} = C_H$ to soil, and there is no sorption of $C_{Hb}$ to soil, as $C_{Hb} = 0$.
For $C_D(x,t) \rightarrow \infty$ (for fixed (x,t)), we find by (10)

$$C_{Hf}(x,t) \rightarrow 0$$

and thus $C_{Hb}(x,t) \rightarrow C_H(x,t)$, i.e.

$$\Psi(x,t,C_H(x,t)) \rightarrow \rho_{\Psi Hb}/\rho_{\Psi H}\ \Psi_{Hb}(C_H(x,t)) \tag{41}$$

Thus locally at (x,t) there is no reduction in sorption of $C_{Hb} = C_H$ to soil, and there is no sorption of $C_{Hf}$ to soil, as $C_{Hf} = 0$. In particular, if there is no sorption of $C_{Hb}$ ($\rho_{\Psi Hb}\Psi_{Hb} \equiv 0$), the total concentration $C_H$ behaves as an inert solute. This was also observed by numerical simulations by *Lafrance et al.* [1989] for the special case considered there. If we restrict to the case of a linear isotherm $\Pi$ (see (25)) the reasoning above can be sharpened by substituting $C_D \rightarrow 0$ by $K_{HD}C_D \rightarrow 0$ and analogously for $C_D \rightarrow \infty$, reflecting the fact, that not only the amount of carrier, but also its sorption capacity influences the process.
The dependence of the effective isotherm for fixed $C_H(x,t)$ on the carrier concentration $C_D$ is shown by

$$d/dC_D\Psi(x,t,C_H) = -\left[\rho_{\Psi Hf}/\rho_{\Psi H}\ \Psi'_{Hf}(C_{Hf}) - \rho_{\Psi Hb}/\rho_{\Psi H} \cdot \Psi'_{Hb}(C_H - C_{Hf})\right] \cdot$$

$$\cdot\ \Pi(C_{Hf})/(1 + C_D(x,t)\Pi'(C_{Hf})) \tag{42}$$

where $C_{Hf} := G(C_D(x,t), C_H)$. The factor after the square brackets has to be interpreted 0 for $C_{Hf} = 0$. Set

$$A(C_H) := \rho_{\Psi Hf}/\rho_{\Psi H} \cdot \Psi'_{Hf}(C_{Hf}) - \rho_{\Psi Hb}/\rho_{\Psi H} \cdot \Psi'_{Hb}(C_{Hb}) \tag{43}$$

Thus the behaviour is determined by the expression A: If $A \geq 0$, then $\Psi$ is monotone decreasing in $C_D$, i.e. an increase of carrier decreases the overall sorption. This is the case if the sorption of free HOC $C_{Hf}$ to soil dominates the sorption of carrier-bound HOC $C_{Hb}$ to soil and this is exactly quantified by the requirement $A \geq 0$. It is this case, which corresponds to an increase in mobility due to the binding of HOC to the carrier. Such a situation is given if there is no sorption of carrier-bound HOC, a case usually considered only in the literature (see section on *special cases*).
If $A \leq 0$, then $\Psi$ is monotone increasing in $C_D$, i.e. an increase of carrier concentration

increases the overall sorption. This is the case if the sorption of $C_{Hb}$ to soil dominates the sorption of $C_{Hf}$ to soil, exactly quantified by the requirement $A \leq 0$. It is this case which corresponds to a decrease in mobility due to the binding of HOC to the carrier. We now turn to the shape of the effective isotherm. Like its constituents, the effective isotherm is monotone increasing in the dissolved concentration $C_H$: We have

$$d/dC_H \Psi(x,t,C_H) = \Big[ \rho_{\Psi Hf}/\rho_{\Psi H} \cdot \Psi'_{Hf}(C_{Hf}) + \rho_{\Psi Hb}/\rho_{\Psi H} \cdot \Psi'_{Hb}(C_D(x,t)\Pi(C_{Hf})) \cdot C_D(x,t)\Pi'(C_{Hf}) \Big] \cdot (1/(1+C_D(x,t)\Pi'(C_{Hf}))), \tag{44a}$$

where

$C_{Hf} := G(C_D(x,t), C_H)$, and $C_D(x,t)$ is fixed.

The factor in round brackets has to be interpreted as 1 for $C_D = C_{Hf} = 0$.
Therefore for fixed (x,t)

$$d/dC_H \, \Psi(x,t,C_H) \geq 0. \tag{44b}$$

More precisely, the slopes of both contributing isotherms $\Psi_{Hf}$, $\Psi_{Hb}$ are weighted by

$$\alpha(x,t,C_{Hf}) := 1/(1+C_D(x,t)\Pi'(C_{Hf})), \tag{44c}$$

i.e. $0 \leq \alpha \leq 1$, and $1-\alpha$, respectively. This shows that not only the values of the single constituents are diminished because of $C_{Hf} \leq C_H$, $C_{Hb} \leq C_H$, but also their slopes. E. g., in the case of no sorption of $C_{Hb}$ ($\rho_{\Psi Hb}\, \Psi_{Hb} \equiv 0$) the effective isotherm lies below $\Psi_{Hf}$ and has a smaller slope.
The overall picture becomes more complicated with respect to the curvature. Even in the case of linear $\Pi$, where the first term of $\Psi$ has the same curvature as $\Psi_{Hf}$ and analogously the second the same as $\Psi_{Hb}$, their interplay can lead to an effective isotherm changing from concave to convex shape and vice versa, also if $\Psi_{Hf}$, $\Psi_{Hb}$ have no change in curvature. In *van Duijn and Knabner* [1992b] this is worked out for the combination of Freundlich isotherms. Another possible reason for the change in curvature is a non-linear $\Pi$. A general discussion can be based on the second derivative of $\Psi$ with respect to $C_H$, computed from (44), but for reasons of briefness, we restrict ourselves to the following example:

$$\Pi(C_{Hf}) = K_{HD} \cdot C_{Hf}^r \text{ with } 0 < r < 1, \tag{45a}$$

i.e there is a strong formation of carrier-bound HOC. If $\Psi_{Hf}(C_{Hf}) = K_{Hf} \cdot C_{Hf}^p$ with $p > 0$ and $\rho_{Hb}\Psi_{Hb} \equiv 0$, i.e. there is only sorption to the soil of the free HOC, then:

For $p \geq 1$, $\Psi$ is strict convex,

for $r < p < 1$, $\Psi$ changes from convex to concave, (45b)

for $p \leq r$, $\Psi$ is strict concave.

If $\Psi_{Hb}(C_{Hb}) = K_{Hb} \cdot C_{Hb}^q$ with $q > 0$ and $\rho_{Hf}\Psi_{Hf} \equiv 0$, i.e. there is only sorption to the soil of the carrier-bound HOC, then:

For $q \geq 1/r$, $\Psi$ is strict convex,

for $1 < q < 1/r$, $\Psi$ changes from convex to concave, (45c)

for $q \leq 1$, $\Psi$ is strict concave.

Strict concavity is a sufficient condition for the existence of travelling waves (see *van Duijn and Knabner* [1992b]. We see, that in (45b) the usual condition $p < 1$ is sharpened to $p \leq r$, showing a stronger dispersion of fronts in this case of enhanced mobility. (45c) can be interpreted in a similar way. We will discuss the existence of travelling waves in detail in a subsequent paper.
If the carrier concentration $C_D$ is constant, the model (12), (13) has the form of the multiple site adsorption model, such that no new features with respect to the shape of concentration profile or breakthrough curves will appear for example in the case of an inflow experiment. If the concentration $C_D$ is space-, but not time- dependent, then again equations (12), (13) have the form of the adsorption model, now for heterogenous porous medium, where the heterogeneity is defined by the carrier profile (if not the porous medium itself is heterogeneous, too). This situation occurs if $C_D$ is a limit profile produced by a constant source, e.g. situated in the surface horizons of a soil. If the concentration $C_D$ depends on time, this situation can be considered as the adsorption model with additional distributed sources or sinks, as

$$d/dt\ \Psi(x,t,C_H) = \partial/\partial C_H\ \Psi(x,t,C_H)\partial_t C_H + \partial/\partial t\ \Psi(x,t,C_H)$$

where the first term is the storage term due to the equilibrium adsorption, whereas the second one can be interpreted as an additional source or sink term of the form

$$\begin{aligned} -\partial/\partial t\ \Psi(x,t,C_H) &= -\partial/\partial C_D\ \Psi(C_D,C_H)\ \partial_t C_D(x,t) \\ &= A(C_H)\ \Pi(C_{Hf})/(1 + C_D(x,t)\Pi'(C_{Hf}))\ \partial_t C_D(x,t) \end{aligned} \tag{46}$$

with A from (43). I.e., whether there is a source or a sink, depends on the sign of $A(C_H)\partial_t C_D$. We first consider situations where $\partial_t C_D \geq 0$, e.g. flow regimes with inflowing carrier $C_D$. This is the situation found commonly in forest soils with DOC

leached from the forest floor material and entering the mineral surface horizons of soils. There is a source exactly for $A \geq 0$, which has been identified above as the case where the sorption of free HOC $C_{Hf}$ dominates the sorption of carrier-bound HOC $C_{Hb}$. There is a sink in the reverse case $A \leq 0$. For $\partial_t C_D \leq 0$, e.g. flow regimes with leaching of initially present carrier, a situation we have to face in agricultural soils, the picture is reversed : a sink for $A \geq 0$ and a source for $A \leq 0$. In the case of an additional source we expect the possibility of local accumulation of the HOC, in the case of an additional sink of local depletion. In paticular, the first case is of paramount importance for risk assessment studies.

## EXTENSIONS AND NUMERICAL APPROXIMATION

In this section we briefly indicate some extensions which we will be the focus of subsequent studies. We end this section with some remarks how to incorporate the developed model into existing codes for the numerical approximation of adsorption models.

If we also want to consider degradation processes, we have to add further sink terms in the right hand side of equation (5a,b), say $h_{Hf}(C_{Hf})$ and $h_{Hb}(C_{Hb})$, respectively. In the transformed model the consequence is a sink term in the right hand side of (13a) in the form

$$h(x,t,C_H) := h_{Hf}(G(C_D(x,t),C_H)) + h_{Hb}(C_H - G(C_D(x,t),C_H)). \tag{47}$$

If we want to include the pore size exclusion effect discussed in the section on *the model*, we can do so by using different water contents $\theta_1$, $\theta_2$ in equation (5a,b) respectively, with $\theta_2 \leq \theta_1$. The reduced water content $\theta_2$ is a consequence of the reduced pore space, which is accessible to the HOC-DOC particles.

If we modify the definition (7) to

$$C_H := C_{Hf} + \theta_2/\theta_1 C_{Hb}, \tag{48}$$

i.e. we use the pore space on which $\theta_1$ is based as a reference, then equation (10) is modified to

$$C_H := C_{Hf} + \theta_2/\theta_1 C_D \Pi(C_{Hf}), \tag{49}$$

The resolution for $C_{Hf}$ for given $C_H$ will again be denoted by G, but is now also (x,t) dependent for (x,t) dependent $\theta_2/\theta_1$, i.e.

$$G = G(x,t,C_D,C_H).$$

The definition of the effective isotherm (12) and rate functions (13) has to be modified correspondingly. Then in the transformed model equation (13a) has to be substituted by

$$\begin{aligned}
&\partial_t(\theta_1 C_H) + \rho_{\Psi H}\,\partial_t\Psi(x,t,C_H) + \rho_{\varphi Hf}\cdot\partial_t S_{Hf} + \\
&+\rho_{\Psi Hb}\partial_t S_{Hb} - \mathrm{div}(\theta_1 D\nabla C_H - qC_H) = \\
&-\mathrm{div}(\theta_1 D\nabla(\theta_2/\theta_1)C_D\Pi(G(x,t,C_H,C_D))) \\
&-\mathrm{div}(q(1-\theta_2/\theta_1)C_D\Pi(G(x,t,C_H,C_D))).
\end{aligned} \tag{50}$$

From the two new terms on the right hand side, the first is only present for space dependent $\theta_2/\theta_1$. Together they can be interpreted as an additional transport term due to convective transport acting on the carrier-bound HOC mass concentration $C_{Hb}$ induced by the 'flow field'

$$\theta_1 D\nabla(\theta_2/\theta_1)+q(1-\theta_2/\theta_1).$$

For space independent $\theta_2/\theta_1$ this is the underlying water flow field reduced in magnitude by the factor $(1-\theta_2/\theta_1)$. This explains the experimentally observed fact of a larger travel speed for the case under consideration compared to inert transport (see e.g. *Enfield et al.*, 1989) without using an unphysical fitting of individual fluxes to experimental data (see the discussion of *Enfield et al.*, 1989 in the section on *special cases*).

One of our main assumptions was the description of the HOC-soil (and HOC-carrier) reactions as adsorption processes without competition. Here we were guided by the limits of experimental information, not of the modelling approach. Instead of the isotherm $\Psi_{Hf}(C_{Hf})$ we could also think of a 'competitive' isotherm $\Psi_{Hf}(C_{Hf}, C_{Hb}, C_D)$, which then would appear in the effective isotherm $\Psi$, with $C_{Hf}$, $C_{Hb}$ substituted by (11,a,b).

We end this paper with some remarks on the numerical approximation of equation (13a-c) with appropriate inital and boundary conditions. A common approach consists of a finite difference discretization in time and then a finite element discretization in space on each time level (e.g. *Knabner*,1992). Depending on the treatment of non-linearities we end up with a set of linear and non-linear equations. For their resolution we must be able to evaluate $\Psi$ and, if we use Newton's method, $\partial/\partial C_H\Psi$.

From (12) and (44) we see that only the evaluation of $C_{Hf}=G(C_D(x,t),C_H)$ is not given by an explicit formula. But for given $C_H$, $C_D$ we can approximate $C_{Hf}$ with minor effect e.g. by applying Newton's method to (10).

## CONCLUSIONS

We have presented a model to describe the transport of a solute in porous medium, which undergoes equilibrium and nonequilibrium adsorption to an immobile sorbent (the soil matrix), but also equilibrium adsorption to a mobile sorbent; e.g. DOC. The carrier itself and the carrierbound fraction of the HOC is allowed to undergo

equilibrium and nonequilibrium adsorption to the soil matrix. We thus have the interplay of the transport with various competing processes: The reduction in mobility due to the adsorption to the soil matrix, a diminishing of this adsorbed fraction and thus an increase in mobility due to the HOC-DOC formation and in addition a reduction in mobility due to the sorption of the carrier-bound HOC.
We have set up a model to incorporate all these processes. By a transformation to a model in terms of total concentrations of HOC and DOC we simplify the model and have a direct expression for the the overall effect of the processes mentioned by means of effective isotherms and rate functions. In this way we are able to identify quantitatively whether we end up with an increase or decrease of mobility. Time dependent carrier concentration can lead to local accumulation or depletion of HOC. The incorporation of pore-size exclusion of the large carrier-bound HOC particles is possible and explains quantitatively a travel speed higher than the interstitial flux.

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# APPENDIX:

HOC: hydrophobic reactive organic chemicals
DOC: dissolved organic carbon
BSM: bulk soil material
PAH: polycyclic aromatic hydrocarbon
PCB: polychlorinated biphenyle
H: HOC, pollutant
D: Carrier molecule, DOC
f: free
b: bound to mobile sorbent
S: mass concentration in immobile phase
$\partial_t$: differentiation with respect to time
$\rho$[M/L$^3$]: density of BSM related to unit volume of porous media
$\theta$[L$^3$/L$^3$]: volumetric water content with respect to unit volume of porous medium
C[M/L$^3$]: mass concentration of solute related to the water filled pore volume
J [M/L$^2$/T]: volumetric flux
P [M/L$^3$/T]: volumetric consumption or production rate
div( $\cdot$ ): divergence operator
x[L],t[T]: variables of space and time respectively
D [L$^2$/T]: matrix of molecular diffusion and mechanical dispersion
q [L/T]: specific discharge
$\rho_{eq}$, $\rho_{neq}$ [M/L$^3$]: bulk density of fractions of the BSM assigned to equilibrium and nonequilibrium sites respectively
$\Psi$, S [M/M]: mass concentration sorbed to equilibrium or nonequilibrium sites respectively, related to fraction of mass of BSM
$\rho_{\Psi Hf}$ [M/L$^3$]: bulk density of the fraction of the BSM providing equlibrium sorption sites for free HOC related to unit volume of porous media
$\rho_{\varphi Hf}$ [M/L$^3$]: bulk density of the fraction of the BSM providing non-equlibrium sorption sites for free HOC related to unit volume of porous medium
$C_{Hf}$ [M/L$^3$]: mass concentration of free HOC dissolved in liquid phase
$S_{Hf}$ [M/M]: mass concentration of free HOC momentary sorbed to the fraction of BSM providing nonequilibrium sites
$\Psi_{Hf}$ [M/M]: mass concentration of free HOC sorbed at equilibrium to the fraction of the BSM providing equilibrium sorption sites
F [M/L$^3$/T]: Rate of loss of mass of free HOC due to the formation of carrier bound HOC
$\rho_{\Psi Hb}$ [M/L$^3$]: bulk density of the fraction of the BSM providing equlibrium sorption sites for carrier-bound HOC
$\rho_{\varphi Hb}$ [M/L$^3$]: bulk density of the fraction of the BSM providing nonequlibrium sorption sites for carrier-bound HOC
$C_{Hb}$ [M/L$^3$]: mass concentration of carrier-bound HOC dissolved in liquid phase
$S_{Hb}$ [M/M]: mass concentration of carrier-bound HOC momentary sorbed to the fraction of BSM providing nonequilibrium sites
$\Psi_{Hb}$ [M/M]: mass of carrier-bound HOC sorbed at equilibrium to the fraction of BSM providing equilibrium sorption sites
$g_{Hf}$ [M/M/T]: reaction rate of the nonequilibrium sorption of free HOC

$g_{Hb}$ [M/M/T]: reaction rate of the nonequilibrium sorption of carrier-bound HOC
$C_H$ [M/L$^3$]: total mass concentration of HOC
$C_D$ [M/L$^3$]: total mass concentration of DOC dissolved in liquid phase
$\Pi(C_{Hf})$ [M/M]: Mass of HOC bound to carrier DOC
G [M/L$^3$]: mass concentration of free HOC in liquid phase in the presence of carrier DOC
$\Psi$ [M/M]: total mass concentration of HOC composed of free and carrier-bound HOC sorbed to equilibrium sorption sites: effective isotherm
$\rho_{\Psi H}$ [M/L$^3$]: sum of bulk densities of fractions providing equilibrium sorption sites for both free and carrier-bound HOC
$f_{Hf}$ [M/M/T]: effective rate function for free HOC sorption to nonequilibrium sites
$f_{Hb}$ [M/M/T]: effective rate function for carrier-bound HOC sorption to nonequilibrium sites
$C_{Db}$ [M/L$^3$]: mass concentration of carrier-bound DOC dissolved in liquid phase
$S_{Db}$ [M/M]: mass concentration of carrier-bound DOC momentary sorbed to the fraction of BSM providing nonequilibrium sorption sites
$C_{Df}$ [M/L$^3$]: mass concentration of free DOC dissolved in liquid phase
$S_{Df}$ [M/M]: mass concentration of free DOC momentary sorbed to the fraction of BSM providing nonequilibrium sites
$g_{Db}$ [M/M/T]: reaction rate of the nonequilibrium sorption of carrier-bound DOC
$g_{Df}$ [M/M/T]: reaction rate of the nonequilibrium sorption of free DOC
$\rho_{\Psi Df}$ [M/L$^3$]: bulk density of the fraction of the BSM providing equilibrium sorption sites for free DOC
$\rho_{\varphi Df}$ [M/L$^3$]: bulk density of the fraction of the BSM providing nonequilibrium sorption sites for free DOC
$\rho_{\Psi Db}$ [M/L$^3$]: bulk density of the fraction of the BSM providing equilibrium sorption sites for carrier-bound DOC
$\rho_{\varphi Db}$ [M/L$^3$]: bulk density of the fraction of the BSM providing nonequlibrium sorption sites for carrier-bound DOC
K, $k_a$, $k_d$: constants
$K_{HD}$ [1]: partition coefficient of HOC between carrier DOC and liquid phase
$K_{Hf}$ [L$^3$/M]: partition coefficient of free HOC between liquid phase and BSM
$K_{Hb}$ [L$^3$/M]: partition coefficient of carrier-bound HOC between liquid phase and BSM
$\varphi_{Hf}$ [M/M]: mass of free HOC sorbed at equilibrium to the fraction of the BSM providing nonequilibrium sites
$\varphi_{Hb}$ [M/M]: mass of carrier-bound HOC sorbed at equilibrium to the fraction of the BSM providing nonequilibrium sites
$k_{Hf}$:rate parameter
$\chi_{Hf}$ [M/M]: sorption isotherm
$\chi_{Hb}$ [M/M]: sorption isotherm

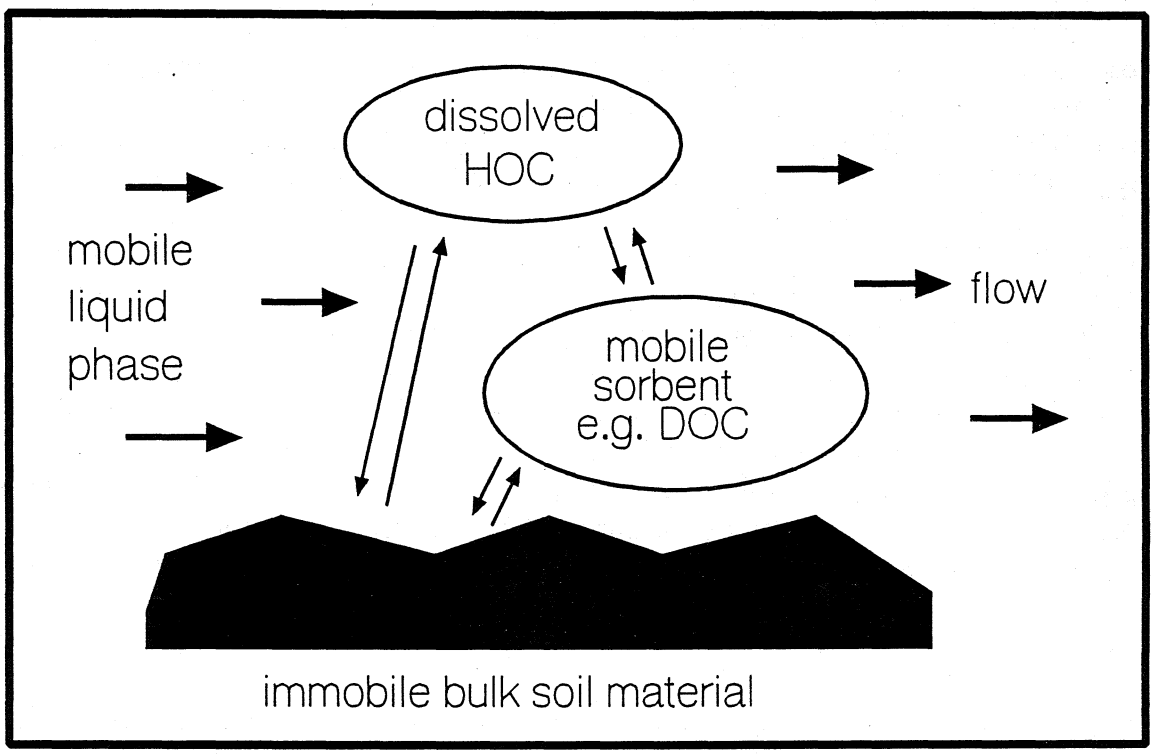


Fig. 1: Three phase system (according to *McCarthy and Zachara*,1989)

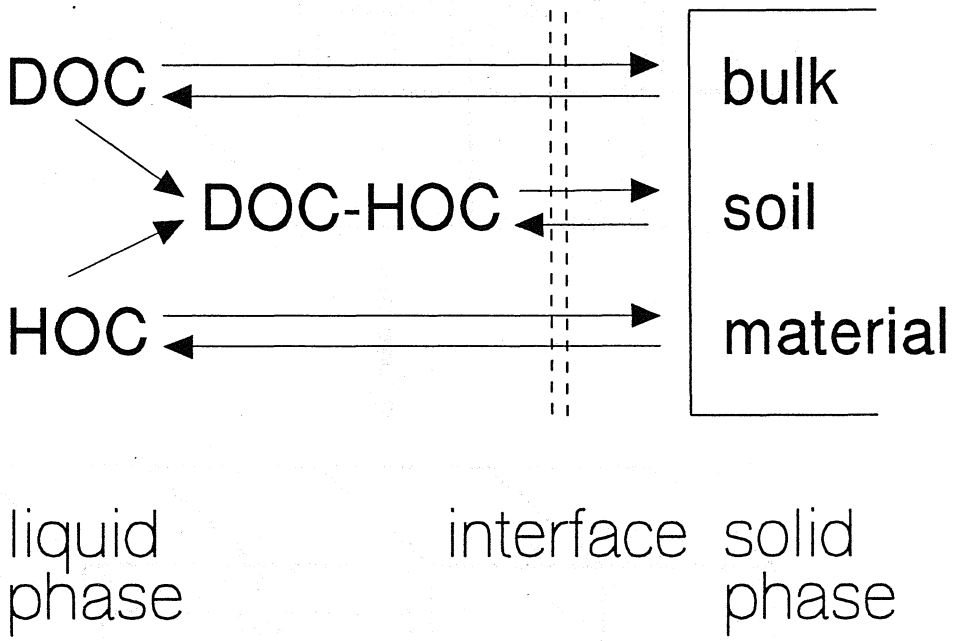


Fig. 2: Reaction pathways considered in the model

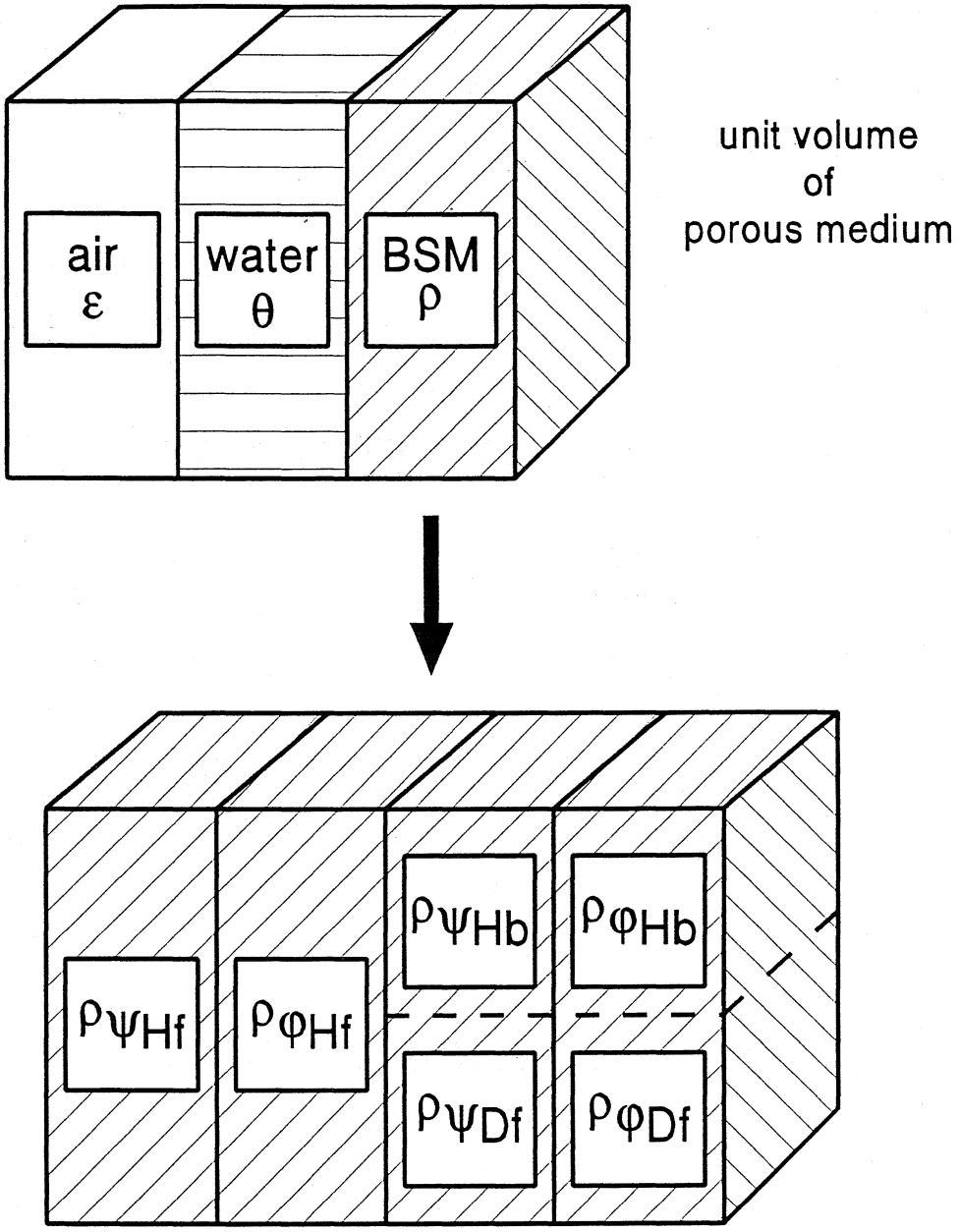


Fig.3: Conceptual fractionation of the BSM into different sorption sites

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